

GRAPHITE AND NITROGEN-FREE CAST ALLOYS

Field of the invention

10 [0001] The present invention is related to alloys for
cast parts, in particular to graphite and nitrogen-free
alloys destined to be structural and /or pressure containing
components for high temperature or low temperature, oxidation
and/or corrosion resistant service such as exhaust systems
15 for gas turbine, gasoline and diesel internal combustion
engines, pumps, valves, fittings, compressors, or other
components. Furthermore, a production process of said alloys
is disclosed.

20 Background of the invention and state of the art

[0002] Conventional Ni-Resist alloys are highly
alloyed austenitic graphitic irons. Carbon levels of the Ni-
Resist alloys are typically in the range of 2.0 to 3.0 weight
percent, and flake or spheroidal graphite is intentionally
25 present in the microstructure.

[0003] The flake graphite alloys, or austenitic grey
irons, were developed in the 1930's. Later, ductile iron was
invented and austenitic ductile iron grades were developed.

[0004] The austenitic ductile irons have superior
30 mechanical properties in comparison to the austenitic grey
irons due to the presence of a spheroidal, or nodular,
graphite morphology, rather than a flake graphite morphology.

The spheroidal graphite particles are less detrimental than flake graphite to the strength and ductility of the alloys. The production of a uniform spheroidal graphite microstructure is more difficult than the production of a flake graphite microstructure. Inadequate process control in the production of austenitic ductile irons can result in a mixed microstructure of flake and spheroidal graphite, with a detrimental effect on expected mechanical properties.

[0005] Good graphite morphology control over varying casting cross sections can be difficult. As the volume/surface area ratio of the casting is increased, it is more difficult to produce spheroidal graphite because of the limited cooling rate. Some cast component designs have drastic variations in transitions between cross sections, which result in difficulties in producing a uniform spheroidal graphite morphology throughout the casting. Some engine exhaust component designs are examples of castings that could benefit from the elimination of the graphite morphology control problem.

[0006] The mechanical properties of such alloys can be further improved and various production problems related to maintaining good graphite morphology can be avoided by the elimination of the graphite. This is one of the purposes of the present invention. The alloy disclosed herein is an alternative for a molybdenum modified ASTM A439 D5B ductile iron alloy.

[0007] For the alloy of the present invention, the carbon levels have been reduced to produce steel rather than cast iron.

[0008] Furthermore, the disclosed alloy is readily weldable, this benefits immediately to downstream manufacturing operations.

5 Aims of the invention

[0009] The present invention aims to provide a substantially graphite and nitrogen-free cast alloy with improved mechanical properties and without diminishment of other desired properties, in particular, corrosion resistance, high temperature strength, oxidation resistance, and non-magnetic characteristics, in comparison with alloys of the prior art. Another aim of the present invention is an easy weldable alloy with a maximum reduction of the coefficient of thermal expansion (CTE) while maintaining a good casting quality

Summary of the invention

[0010] The present invention discloses an air melted, substantially graphite and nitrogen-free alloy, aged or not aged by precipitation hardening, specially adapted for gas turbine or internal combustion engine exhaust system parts, comprising a graphite-free microstructure of the following composition:

	Carbon	max 0.4 wt. %
25	Silicon	0.5 to 5.5 wt. %
	Manganese	0.1 to 1.5 wt. %
	Phosphorous	0.01 to 0.08 wt. %
	Nickel	13 to 38 wt. %
	Chromium	0.50 to 6.00 wt. %
30	Sulphur	max 0.12 wt. %
	Nitrogen	max 0.02 wt. %

Iron balance

[0011] Additionally, the present invention discloses a composition further comprising:

Molybdenum in the range of 0,1 to 4 wt.%

5 [0012] Additionally, the present invention discloses a composition further comprising maximum 1 wt.% of copper.

[0013] Additionally, the present invention discloses a composition further comprising Copper in a range of 0.5 to 8 wt.% and wherein the nickel concentration is in a range of 13

10 to 22 wt.%

[0014] In a particular embodiment of the present invention, the composition further comprises

Niobium 1 to 5 wt.%

Titanium max 1 wt.%

15 Aluminium max 1 wt.%

[0015] In another particular embodiment of the present invention, the composition further comprises

Niobium max 2 wt.%

Tungsten max 4 wt.%

20 Zirconium max 1 wt.%

Vanadium max 1 wt.%

[0016] Additionally a process for the manufacturing of the composition is disclosed wherein said alloy is strengthened by precipitation hardening of $(\text{Ni}_3[\text{Al}, \text{Ti}])$,

25 $(\text{Ni}_3[\text{Nb}, \text{Al}, \text{Ti}])$, or (Ni_3Nb) .

[0017] In a particular embodiment of the present invention a process for the manufacturing of the composition is disclosed wherein said alloy is strengthened by precipitation hardening of Mo_2C .

30 [0018] In another particular embodiment, the process for the manufacturing of the composition of the present

invention is disclosed wherein said alloy is not strengthened by ageing and precipitation hardening.

Detailed description of the invention

5 [0019] In some applications the desired graphite-free microstructure is produced by restricting the carbon content of the alloy to very low levels, so that they are essentially carbon-free versions of the alloy. In other applications solid solution strengthening of the alloys by interstitial
10 carbon is desirable. Carbon contents up to the solubility limit for each specific composition are foreseen. The graphite-free alloys of the present invention are classified as high alloy steels rather than cast irons.

[0020] The advantages of ASTM A439-83 and ASTM A436-84
15 alloys in comparison to conventional cast irons are corrosion resistance, high temperature strength, oxidation resistance, and non-magnetic properties for some grades. None of these attributes should be affected by the elimination of graphite from the microstructure. The matrix of the conventional Ni-
20 Resist alloy is targeted as closely as possible to insure that these attributes are preserved.

[0021] A modified D5B alloy containing 1 wt.% Mo was selected for the initial experiments. A carbon-free version of this initial composition was produced. This alloy was
25 designated DX35BM for experimental identification.

Modified D5B composition (D5Bw/Mo)

Carbon	2.4 wt.%
Silicon	1-2.8 wt.%
Manganese	max 1 wt.%
30 Phosphorus	max 0.08 wt.%
Nickel	34-36 wt.%

Chromium max 0.1 wt.%

Molybdenum 1 wt.%

Iron balance

Carbon-free DX35BM composition following the present
invention

Carbon max 0.1 wt.%

Silicon 1.00 to 2.8 wt.%

Manganese max 1.00 wt.%

Phosphorous max 0.04 wt.%

10 Nickel 34 to 36 wt.%

Chromium 2.00 to 3.00 wt.%

Molybdenum 0.7 to 1 wt.%

Sulphur max 0.04 wt.%

Iron balance

15 [0022] Trial heats of DX35BM were produced with a carbon level of 0.01 wt.%. The mechanical property results for the carbon-free DX35BM alloy are exceptional. Both tensile strength and elongation meet the mechanical properties specification of the exhaust system, with the
 20 elongation result exceeding the specification minimum by a large margin. The yield strength and hardness however, are lower than the specification minimum. Trial heats with a carbon level of 0.1 wt.% indicated that the exhaust system minimum yield strength is achievable with a modest increase
 25 in carbon level. The carbon level had to be increased further to achieve the specification minimum for hardness.

[0023] Another test heat was made with an aim carbon level of 0.25 wt.%. All the mechanical properties for this heat met the exhaust system parts specification requested for
 30 D5B w/Mo alloys, exceeding the minimum requested values by a comfortable margin.

[0024] This increase in carbon content is enough to increase the yield strength and hardness of the matrix, but below levels that would result in a graphitic second phase in the microstructure.

5 Graphite-free DX35BM composition

	Carbon	0.2 to 0.4 wt.%
	Silicon	1.00 to 2.8 wt.%
	Manganese	max 1.00 wt.%
	Phosphorous	max 0.04 wt.%
10	Nickel	34 to 36 wt.%
	Chromium	2.00 to 3.00 wt.%
	Molybdenum	0.7 to 1 wt.%
	Sulphur	max 0.04 wt.%
	Iron	balance

- 15 [0025] Two tables have been prepared, one of typical mechanical properties of D5, D5B, and DX35BM, and one of elevated temperature properties of D5B, D5B+Mo, and DX35BM.

Typical Mechanical Properties of Ni-Resist Type Alloys			
	Type D-5	Type D-5B	DX35BM
Tensile strength, ksi	55-60	55-65	80-95
Yield strength, ksi (0.2wt.% offset)	30-35	30-35	40-45
Elongation, wt.% in 2"	20-40	6-12	20-40
Proportional limit, ksi	9.5-11	10.5-13	-
Elastic modulus, psi * 10 ⁶	16-20	16-17.5	18-22
Hardness, BHN	130-180	140-190	140-170

Elevated Temperature Properties Comparison				
Data Source		DIS	DIS	WA
Alloy		D5B	D5B+Mo	DX35BM
Tensile strength, ksi				
	70 F	60,8	61,2	86,6
	1000 F	47,2	48,8	67,0
	1200 F	40,6	46,4	-
	1400 F	24,9	31,1	-
Yield strength, ksi				
	70 F	41,0	41,0	41,6
	1000 F	25,8	28,6	30,0
	1200 F	24,2	29,9	-
	1400 F	18,6	24,3	-
Elongation, wt.%				
	70 F	7,0	7,5	26,0
	1000 F	9,0	7,5	58,0
	1200 F	6,5	6,5	-
	1400 F	24,5	12,5	-

[0026] The coefficient of thermal expansion and elastic modulus of DX35BM are close to those of D5B w/Mo over the operating temperature range of the engine. This is an important factor in this application of the alloy due to
5 thermal stress considerations.

[0027] The properties at room temperature were significantly improved, but the advantage of DX35BM over D5B w/Mo diminished with increasing temperature. The tensile properties of DX35BM at 540°C (1000°F) only slightly exceed
10 those of D5B (w/Mo). These results were confirmed by the trial of a test part and DX35BM could be a potential direct replacement for D5B (w/Mo).

[0028] DX35BM offers comparable mechanical and physical properties to D5B w/Mo, while eliminating any
15 potential problems with graphite morphology control.

[0029] The conventional D5B (w/Mo) alloy which can be replaced by the alloy of the present invention, is not considered as a weldable alloy. One of the goals of the present invention was to produce an alloy that was easily
20 weldable. A weldable alloy facilitates the repair of defects uncovered during the manufacturing process, lowers scrap rates and manufacturing costs.

[0030] A further improvement disclosed in the present invention is a nitrogen-restricted version of the above
25 disclosed DX35BM alloy. The motivation of such a low nitrogen DX35BM alloy is to assure internal soundness and the avoiding of surface pinholing defects.

[0031] In low carbon containing alloys, nitrogen absorption and content of the melt is not suppressed by high
30 levels of carbon in solution, for this reason, the alloy of the present invention can be produced with raw materials of

low nitrogen content. Other ways to achieve low nitrogen levels are melting practices that avoid nitrogen pick up from the atmosphere and refining processes that remove nitrogen from the melt. Non-limitative examples of such practices and processes are inert gas protection, the timing of bulk chromium additions, Argon Oxygen Decarburization (AOD) refining, and furnace and ladle refining using special composition nitrogen removing slag. These practices and processes may be applied both jointly and separately. The alloy of this embodiment of the present invention typically deals with nitrogen levels between 0.002 wt% and 0.01 wt%. In the solidified alloy, the nitrogen level should not exceed 0.02 wt%. Nitrogen levels in excess of 0.02 wt% in said alloys lead to greater amounts of upgrade and weld repair, which are not desired by the customer.

[0032] Another approach for producing better parts at slightly higher nitrogen levels is the addition of quantities of nitride formers. Non limitative examples of such nitride former are Ti, V or Zr. Nevertheless, these elements influence the CTE of the alloy and should be limited to a maximum amount of 1%, and preferably 0.5%.

[0033] The inventor developed and refined gas metal arc welding (GMAW) and gas tungsten arc welding (GTAW) procedures for DX35BM using commercially available weld wires containing an approximately the same level of nickel.

[0034] The aim of the present invention is a substantially graphite and nitrogen free alloy with improved room temperature mechanical properties that can be substituted directly for similar austenitic ductile and grey cast irons. A second aim of the present invention is modified versions of DX35BM with higher strengths at 540-700°C

(1000°F-1300°F). Higher strengths at these temperatures would allow the operating temperature of the engine to be increased, and improves the efficiency.

[0035] The strengthening mechanism to improve the high
5 temperature strength of a modified DX35BM alloy is precipitation hardening (PH). Distinctly different precipitation hardening mechanisms have been investigated, in distinctly different modifications of the alloy.

[0036] A first embodiment of the present invention is
10 a graphite and nitrogen free version of DX35BM that is a demonstrated replacement for ASTM A439 D5-B w/Mo.

[0037] A second embodiment of the present invention is a graphite free, precipitation hardened version of DX35BM strengthened by the controlled precipitation of Mo_2C carbide.

15 [0038] A review of sections of the Fe-C-Mo ternary phase diagram at 2 wt.% and 4 wt.% Mo indicates that Mo_2C carbide is the equilibrium carbide at approximately 0.25 wt.% C, up to nearly 750°C (1400°F). This provides a basis for the investigation of the Mo_2C precipitation reaction in DX35BM
20 and its use as a stable second phase for precipitation hardening in the desired service temperature range of 650-700°C (1200°-1300°F).

[0039] The desired chemical composition is coupled with appropriate heat treatment cycles to achieve the desired
25 precipitation hardening effect. The heat treatment cycle originally applied to the DX35BM alloy is a stabilisation heat treatment for elevated temperature service similar to that used for D5B+Mo. The unmodified alloy in the solution annealed condition responds to ageing treatments, even if not
30 as optimally as a higher alloyed modification of the composition. The solution annealing + ageing heat treatment

produces enough precipitation hardening to improve mechanical properties, especially in the 540-700°C (1000° - 1300°F) range.

[0040] In the same way, other carbide forming elements
5 can be added in the alloy to perform with the precipitation hardening reinforcement like tungsten, vanadium, zirconium, and niobium in percentages up to 4 wt.% each.

[0041] A further embodiment of the present invention
is a higher Mo graphite-free precipitation hardened DX35BM
10 alloy strengthened by the controlled precipitation of Mo₂C. By only raising the DX35BM molybdenum content to 2 to 4 wt.%, the inventor was able to exploit enhanced precipitation hardening by Mo₂C precipitation.

[0042] An additional embodiment of the present
15 invention is a graphite-free version of DX35BM containing Nb and additions of titanium and aluminium.

[0043] This alloy is strengthened by the precipitation
of various phases including: gamma prime, γ' (Ni₃[Al,Ti]),
gamma double prime, γ'' (Ni₃[Nb,Al,Ti]), and delta, δ (Ni₃Nb),
20 with Nb rich γ'' and δ being the intended secondary phases for strengthening. The proposed alloy contains 0.02 wt.% maximum carbon and about 4 wt.% Nb. The very low carbon content is required to minimise the formation of Nb carbides. The DX35BM silicon content is lowered to less than 1.0 wt.% to minimise
25 the formation of Nb silicides.

[0044] The Al and Ti additions typically used for the
formation of predominantly γ' and γ'' secondary phases result
in a very oxidation sensitive melt. For that reason, melts of
 γ'/γ'' strengthened alloys are almost universally melted and
30 poured in vacuum or inert atmosphere furnaces. Al and Ti are

5 routinely used in the foundry as deoxidisation additions, but at relatively low levels in the final composition of air melted alloys. The Al and Ti level typically used for the formation γ' and γ'' are not very desirable from a foundry perspective. The Al and Ti contents of the proposed alloy are both limited to 1 wt.% maximum to facilitate melting in air.

[0045] Another embodiment of the present invention is a graphite-free alloy from a carbon-free version of D5S. The graphite-free version of D5S is a carbon-free version of the
10 alloy with less than 0.10wt.% carbon, because the high silicon content of D5S limits carbon solubility in the matrix.

Composition of D-5S

	Carbon	2.3 wt.%
15	Silicon	4.9-5.5 wt.%
	Manganese	max 1 wt.%
	Phosphorus	max 0.08 wt.%
	Nickel	34-37 wt.%
	Chromium	max 1.75-2.25 wt.%
20	Iron	balance

Composition of DX35S

	Carbon	max 0.1 wt.%
	Silicon	4.9-5.5 wt.%
	Manganese	max 1 wt.%
25	Phosphorus	max 0.08 wt.%
	Nickel	34-37 wt.%
	Chromium	max 1.75-2.25 wt.%
	Nitrogen	max 0.02 wt.%
	Iron	balance

30 [0046] A further embodiment of the present invention is a graphite-free copper bearing alloy as a substitute of

Ni-Resist Type 1 and Type 1b which are grey iron alloys of the prior art containing 13.5 to 17.5 wt.% nickel and 5.5 to 7.5 wt.% copper. These alloys are typically adapted to producing pump and valve components.

5 Ni-Resist Type 1

	Carbon	max 3 wt.%
	Silicon	1.00 to 2.8 wt.%
	Manganese	0.5 to 1.5 wt.%
	Nickel	13.5 to 17.5 wt.%
10	Copper	5.5 to 7.5 wt.%
	Chromium	1.5 to 2.5 wt.%
	Iron	balance

Ni-Resist Type 1b

	Carbon	max 3 wt.%
15	Silicon	1.00 to 2.8 wt.%
	Manganese	0.5 to 1.5 wt.%
	Nickel	13.5 to 17.5 wt.%
	Copper	5.5 to 7.5 wt.%
	Chromium	1.75 to 3.5 wt.%
20	Iron	balance

[0047] These compositions cannot be produced as ductile iron because the copper interferes with the formation of nodular graphite. The improvement in mechanical properties between the flake graphite conventional alloy and a graphite-free version DX16 following the present invention is significant.

DX16

	Carbon	max 0.4 wt.%
	Silicon	max 2.8 wt.%
30	Manganese	max 1.5 wt.%
	Nickel	13 to 18 wt.%

Copper	5 to 8 wt.%
Chromium	1.5 to 3.5 wt.%
Nitrogen	max 0.02 wt.%
Iron	balance

- 5 [0048] An additional embodiment of the present invention is a graphite-free copper bearing alloy as a substitute of Ni-Resist Type 6 which is a grey iron alloy of the prior art containing 18 to 22 wt.% nickel and 3.5 to 5.5 wt.% copper. This alloy is typically adapted to producing pump and valve components.

Ni-Resist Type 6

Carbon	max 3 wt.%
Silicon	1.50 to 2.50 wt.%
Manganese	0.5 to 1.5 wt.%
15 Nickel	18 to 22 wt.%
Copper	3.5 to 5.5 wt.%
Chromium	1.0 to 2.0 wt.%
Molybdenum	max 1.0 wt.%
Iron	balance

- 20 [0049] This composition cannot be produced as ductile iron because the copper interferes with the formation of nodular graphite. The improvement in mechanical properties between the flake graphite conventional alloy and a graphite-free version DX20 following the present invention is significant.

DX20

Carbon	max 0.4 wt.%
Silicon	max 2.50 wt.%
Manganese	max 1.5 wt.%
30 Nickel	18 to 22 wt.%
Copper	3 to 6 wt.%

Chromium	1.0 to 2.0 wt.%
Molybdenum	max 1.0 wt.%
Nitrogen	max 0.02 wt.%
Iron	balance

5 [0050] Examples of compositions according to the present invention

Example 1

Carbon	max 0.4 wt.%
Silicon	max 2.8 wt.%
10 Manganese	max 1.00 wt.%
Phosphorous	max 0.04 wt.%
Nickel	34 to 38 wt.%
Chromium	0.50 to 3.00 wt.%
Molybdenum	0.5 to 4 wt.%
15 Tungsten	max 4 wt.%
Niobium	max 2 wt.%
Zirconium	max 1 wt.%
Vanadium	max 1 wt.%
Sulphur	max 0.04 wt.%
20 Nitrogen	max 0.02 wt.%
Iron	balance

Example 2

Carbon	max 0.1 wt.%
Silicon	4.90 to 5.5 wt.%
25 Manganese	max 1.00 wt.%
Phosphorous	max 0.08 wt.%
Nickel	34 to 38 wt.%
Chromium	1.75 to 2.25 wt.%
Molybdenum	max 2 wt.%
30 Sulphur	max 0.04 wt.%
Nitrogen	max 0.02 wt.%

Iron balance

Example 3

Carbon max 0.4 wt. %

Silicon max 2.8 wt. %

5 Manganese max 1.5 wt. %

Phosphorous max 0.04 wt. %

Nickel 13 to 18 wt. %

Chromium 2.00 to 3.00 wt. %

Molybdenum max 2 wt. %

10 Copper 5 to 8 wt. %

Sulphur max 0.04 wt. %

Nitrogen max 0.02 wt. %

Iron balance

Example 4

15 Carbon max 0.4 wt. %

Silicon max 2.5 wt. %

Manganese max 1.5 wt. %

Phosphorous max 0.04 wt. %

Nickel 18 to 22 wt. %

20 Chromium 1.00 to 3.00 wt. %

Molybdenum max 2 wt. %

Copper 3 to 6 wt. %

Sulphur max 0.04 wt. %

Nitrogen max 0.02 wt. %

25 Iron balance

Example 5

Carbon max 0.10 wt. %

Silicon max 1.00 wt. %

Manganese max 1.00 wt. %

30 Phosphorous max 0.04 wt. %

Nickel 34 to 38 wt. %

	Chromium	0.5 to 3.0 wt.%
	Niobium	1 to 5 wt.%
	Titanium	max 1 wt.%
	Aluminium	max 1 wt.%
5	Sulphur	max 0.04 wt.%
	Nitrogen	max 0.02 wt.%
	Iron	balance